SYNTHESIS, CHARACTERIZATION AND ACTIVITY OF Al-MCM-41 CATALYST FOR HYDROXYALKYLATION OF EPOXIDES

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Dedication to my beloved father, mother, family and friends…

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ABSTRACT

Perfumery chemicals and intermediates are produced on a large scale by Friedel Crafts alkylation or acylation of aromatic compounds in the presence of Lewis acid catalyst. However, problem in the industrial process of perfumery chemical and intermediate manufacture like toxity, corrosivity and production of pollutants, make convenient to change the conventional Lewis acid $AlCl_3$ or $FeCl_3$ catalysts by acid solid catalyst. Thus, Al-MCM-41 catalysts were prepared with various SiO_2:Al_2O_3 ratios via direct and secondary syntheses using sodium aluminate as the aluminium source. Al-MCM-41 was characterized by X-ray Diffraction (XRD), Surface Area Analyzer Instrument and Fourier Transform Infrared Spectroscopy (FTIR). The results indicate that Al-MCM-41 sample with a uniform hexagonal pore structure and high surface area was synthesized. Structural studies by ^{27}Al and ^{29}Si MAS NMR spectroscopy indicated that Al are in the tetrahedral form and located in the framework. The presence of distorted framework aluminium was also observed, more significantly in the secondary aluminated samples. Maximum amount of Al was incorporated by direct synthesis with SiO_2:Al_2O_3 ratio of 10 and a calculated Si/Al ratio of 15.2. Acidity studies using Pyridine Desorption Measurement and Temperature Programmed Desorption of Ammonia (TPD-NH_3) show that the acidity of Al-MCM-41 increases with increase in Al incorporation into the MCM-41 framework. The potential of H-Al-MCM-41; as a heterogeneous catalyst was studied in the hydroxyalkylation of benzene with propylene oxide as a model reaction. Favourable reaction conditions such as SiO_2:Al_2O_3 ratios, temperature, time on stream, the reactant mole ratio and solvent have significant influence on the distribution of products. Gas chromatography analysis indicates that H-Al-MCM-41 with SiO_2:Al_2O_3 ratio of 10 demonstrates the highest catalytic activity with a conversion of benzene and selectivity of 92.3% and 87.5% respectively. The formation of 2-phenyl-1-propanol was favourable occurred at a temperature of 393 K after 24 hours with propylene oxide to benzene mole ratio of 0.5 using nitrobenzene as the solvent. The activity enhancement for catalyst is associated with the presence of distorted tricoordinated aluminium as Lewis acid sites. The strength of Lewis acid sites was correlated to appropriate aluminium content, temperature, B/L ratio, crystallinity and surface area of sample which played a role in order to improve catalytic activity of Al-MCM-41. Aprotic dipolar solvent such as nitrobenzene stabilized the unstable intermediate of propoxy cations to prevent propylene oxides oligomerisation. The results indicate that instead of aluminium content, solvent and reactant mole ratio also play a role to give high conversion and selectivity of 2-phenyl-1-propanol.

ABSTRAK

Bahan kimia dan perantaraan pewangi biasanya dihasilkan pada skala yang besar melalui tindak balas pengalkilan dan pengasilan sebatian aromatik dengan mangkin asid Lewis. Masalah yang timbul dalam proses industri pengeluaran bahan kimia dan perantaraan pewangi seperti ketoksikan, kakisan dan penghasilan sisa adalah bertepatan dengan menggantikan mangkin asid Lewis konvensional $AlCl_3$ atau $FeCl_3$ kepada mangkin pepejal berasid. Maka, mangkin Al-MCM-41 disediakan dengan pelbagai nisbah SiO_2:Al_2O_3 melalui sintesis terus dan sekunder menggunakan natrium aluminat sebagai sumber aluminium. Al-MCM-41 telah dicirikan menggunakan teknik Pembelauan Sinar-X (XRD), Analisis Luas Permukaan dan Spektroskopi Inframerah. Keputusan menunjukkan Al-MCM-41 mempamerkan struktur liang heksagon yang seragam dengan luas permukaan yang tinggi. Kajian struktur oleh Spektroskopi ^{27}Al dan ^{29}Si Putaran Sudut Ajaib-Resonans Magnet Nukleus (PSI-RMN) menunjukkan aluminium hadir dalam bentuk tetrahedral dan terletak dalam rangka struktur. Kehadiran rangka struktur aluminium terherot juga dapat diperhatikan lebih signifikan dalam sampel sintesis secara sekunder. Kandungan maksimum aluminium memasuki bingkaian dipamerkan oleh sampel dengan nisbah SiO_2:Al_2O_3 bersamaan 10 dan Si/Al dihitung bersamaan 15.2. Kajian keasidan dijalankan menggunakan Penjerapan Piridina dan Penyahjerapan Ammonia Suhu Teraturcara (TPD-NH_3) menunjukkan keasidan Al-MCM-41 meningkat dengan penambahan aluminium ke dalam bingkaian MCM-41. Maka, potensi mangkin H-Al-MCM-41 dalam tindak balas Friedel-Crafts diuji ke atas tindak balas penghidroksialkilan benzena dengan propilena oksida sebagai tindak balas model. Taburan hasil tindak balas didapati bergantung kepada keadaan terbaik tindak balas seperti nisbah SiO_2:Al_2O_3, suhu tindak balas, masa tindak balas, nisbah mol reaktan dan pelarut. Analisis kromatografi gas menunjukkan H-Al-MCM-41 dengan nisbah SiO_2:Al_2O_3 bersamaan 10 mempamerkan aktiviti permangkinan yang tinggi dengan darjah penukaran benzena dan kepilihan masing-masing 92.3% dan 87.5%. 2-fenil-1-propanol terhasil pada kadar terbaik pada suhu 393 K selepas 24 jam dengan nisbah mol propilena oksida kepada benzena bersamaan 0.5 dengan nitrobenzena sebagai pelarut. Peningkatan aktiviti permangkinan sampel ini dikaitkan dengan kehadiran aluminium trikoordinatan terherot sebagai tapak asid Lewis. Kekuatan tapak asid Lewis dikaitkan dengan kandungan aluminium, suhu, nisbah B/L, kehabluran dan luas permukaan sampel yang berperanan meningkatkan aktiviti permangkinan Al-MCM-41. Pelarut dwipolar aprotik seperti nitrobenzena dapat menstabilkan bahan perantaraan ion propoksi bagi mengelakkan pengoligomeran propilena oksida. Keputusan menunjukan selain daripada kandungan aluminium dalam sampel, pelarut dan nisbah reaktan juga memainkan peranan dalam meningkatkan darjah penukaran dan kepilihan 2-fenil-1-propanol.

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B/L ratio	-	Brønsted acid sites to Lewis acid sites ratio
BET	-	Brunnauer, Emmett and Teller
Cu K_α	-	X-ray diffraction from Copper K energy levels
FTIR	-	Fourier Transform Infrared Spectroscopy
GC-MS	-	Gas Chromatography- Mass Spectroscopy
h	-	Hour
IS	-	Internal Standard
IUPAC	-	International Union of Pure and Applied Chemistry
KBr	-	Potassium Bromide
MAS NMR	-	Magic-Angle-Spinning Nuclear Magnetic Resonance
N_2	-	Nitrogen
OH	-	Hydroxyl
P/P_o	-	Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure P_o of the adsorbate at the temperature where the isotherm is measured
SiO_2: Al_2O_3	-	Silica to Alumina ratio
SiO_4	-	Siliceous; framework silicon in zeolite
T	-	Reaction Temperature
TO_4	-	Tetrahedral unit where T= Al or Si
XRD	-	X-ray Diffraction technique
λ	-	Wavelength
2θ	-	Bragg Angle

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

The concept of catalysis was first discovered by Berzelius in 1836. The word catalysis came from combination of two Greek words, κατα (kata) and λυδειν (lysein) which was defined as 'loosening down' [1]. The phenomenon of catalysts has been extensively studied since the early decades of the 19th century, and used unconsciously for a much larger period. Nowadays, the catalyst market is seeing moderate growth especially in fine chemicals and environmental markets sectors which posesses higher perfoming. Meanwhile polymerization catalysts are growing at more moderate rate, whereas refining and petrochemical catalysts are experiencing low to flat growth. According to Comyns [2], the global catalyst market had a volume of $10.5 billion in 2001 and is expected to grow to almost $13.5 billion or 4.6% per year by 2007. Environmental catalysts are the biggest segment in the merchant, accounting for 27% of 2001 market. Polymerization catalysts are second with nearly 22%, followed by refining (21%), petrochemical (20%) and fine chemical and intermediates (10%). However, fine chemical and environmental sectors are expected to grow at near or above 8% per year for the next 6 years. The use of combinatorial catalyst for discovery and optimisation of catalytic performance is expected to have a significant effect on the rate at which new catalysts are

developed [3, 4]. Basically catalyst can be classified into two types which are homogeneous and heterogeneous catalyst. Homogeneous catalyst particularly Lewis acid catalyst is well known and has been applied in Friedel-Crafts alkylation and acylation reactions. However, new policies were introduced involving the applications of homogeneous catalysts as a result of the problems caused by them; such as corrosion, loss of catalyst and disrupting the environment [5]. The policies focused on environment protection and avoidance of unfriendly reactants and catalysts with better selectivity in order to minimize product waste and expensive separations and recycling [6]. Meanwhile, heterogeneous catalysts such as molecular sieves, zeolites and porous materials for liquid phase organic synthesis reactions can give a lot of benefits such as clean reaction product solution after filtration, ease of recovery and avoidance of corrosion. Therefore, development of efficient heterogeneous catalysts is interesting and useful especially in the production of fine chemical and intermediates.

1.2 Research Background

Recently, many perfume chemical and intermediates are produced on a large scale by Friedel Crafts reactions. The reaction usually involves the alkylation or acylation of an aromatic compound in the presence of Lewis acid catalyst. For example, the Friedel Crafts alkylation of benzene with ethylene oxide is a commercial route to produce β-phenethyl alcohol or 2-phenyl-ethanol. 2-phenyl-ethanol is an important intermediate which is used because of its exquisite odour of natural rose petal [7]. On the other hand, the alkylation of 2-methoxynapthalene with propylene oxide is the preferred method to produce a precursor for non-steroidal, anti-inflammatory agent naproxen [8, 9]. Basically, aluminium chloride is the most common catalyst in the Friedel Crafts alkylation instead of sulphuric acid, phosphoric acid, ferric chloride and boron trifluoride. The common alkylation agents are olefin, alkyl halide, alcohol and epoxides [10].

The reaction of benzene or alkylbenzene with epoxides in the presence of some homogeneous Lewis acid was first reported by Hata *et al.* [11]. Next, Nakajima *et al.* [12] studied stereospecific Friedel-Crafts alkylation of benzene with propylene oxide by aluminium chloride as Lewis acid catalyst and stereochemistry of ring opening of epoxides. In 1970s, asymmetric induction in the Friedel-Crafts reaction of benzene with (+)-1, 2-epoxybutane was studied by Nakajima *et al.* [13]. Meanwhile, Inoue *et al.* [14] examined the reaction of toluene and anisole with 2-methoxyoxirane and 2, 3-dimethyloxirane in the presence of aluminum chloride as Lewis acid. Later, in the 80s, $SnCl_4$ as catalyst on stereoselective Friedel-Crafts alkylation via epoxide transannular and cycloalkylation reactions were studied [15, 16].

1.3 Problem Statement

Basically, introduction of hydroxyl group into an aromatic compound using ethylene or propylene oxides are relatively well established in the presence of Lewis acid catalysts. However, the selectivity of hydroxyalkylated products were affected by side reactions such as epoxide oligomerisation or further reaction of the hydroxyalkylated intermediate with the starting reactant to yield bisarylalkane derivates.

Hence, a cleaner alternative process which is truly catalytic is needed due to serious effluent problem associated with the use of a stoichiometric amount of $AlCl_3$ and the corrosive reaction conditions. A lot of current processes in the production of fine chemicals and intermediates are using homogeneous catalyst. The manufacture of fine chemicals and intermediates involving the batch processes, are associated with the production of large quantities of toxic waste [17]. Homogeneous catalysts such as mineral acid, strong base and toxic metal reagent impose many drawback including handling difficulties, inorganic contamination of organic products, the formation of large volume of toxic waste and poor reaction selectivity leading to unwanted isomers and side products [18].

In the hydroxyalkylation of aromatic with epoxides, the epoxides was added into a suspension of anhydrous $AlCl_3$ in the aromatic subtracts [19]. The postulated mechanism of hydroxyalkylation proposed that aluminium chloride form an addition compound with the epoxide which preferably opens at the most substituted carbon atom [12]. As a result, a very reactive intermediate forms and reacts rapidly with the aromatic and another molecule of epoxide. In this reaction, the tendency of epoxide oligomerisation decreases due to dilution of epoxide [11]. The attack of the aromatic gives rise to the formation of an alcohol-$AlCl_3$ complex [20]. The complex is generally soluble in the aromatic and is therefore more available than the unreacted suspended $AlCl_3$. The alcohol-$AlCl_3$ complex becomes an increasingly important negative factor since it is a polymerization catalyst for the epoxide [7]. Therefore, a stoichiometric amount or excess of aluminium chloride and large excess of the aromatic are needed to prevent oligomerisation of the epoxide. The complex has to be decomposed with water in order to obtain the desired product. The reaction and work-up also should occur below 25ºC; otherwise the alcohol-$AlCl_3$ complex will react further with another aromatic molecule to afford 1, 2-diaryalkanes [21]. Furthermore, $AlCl_3$ catalyzed hydroxyalkylation requires a hydrolysis step resulting in a hydrated $AlCl_3$ waste stream. As a result, the catalyst is not reusable [14].

Extensive studies were conducted on alkylation and hydroxyalkylation of aromatic using heterogeneous catalyst as a model reaction [22-26]. However, zeolites such as H-ZSM-5, modernite, H-Beta and ZnNaY catalysed intermolecular hydroxyalkylation of epoxides are very difficult because of competing epoxide oligomerisation and rearrangement [21]. The main limitation of zeolites is the range of pore sizes available. The small pore size of zeolites prevent it from being useful in new applications with bulky and large molecule such as polymerization. Besides, the cations present inside the structure may in some cases obstruct the pore apertures and limit the rate of reactions [27]. In some cases for example, the formation of coke which is deposited inside the pore of zeolite can hinder the normal diffusion of reactants and products in and out of the catalyst [28, 29]. For this reason, in the past, efforts were directed towards the synthesis of similar structures which led to the discovery of MCM-41 [30]. Thus, the recent synthesis of mesoporous molecular sieves MCM-41 has expanded the capabilities of heterogeneous catalyst. Compared to zeolites, mesoporous MCM-41 materials is a useful candidate.

1.4 Research Objectives

The objectives of this research are:

1. To synthesize and characterize mesoporous Al-MCM-41 with different SiO_2:Al_2O_3 ratios through direct and secondary synthesis.
2. To study acidity properties of aluminium containing MCM-41.
3. To investigate the catalytic activity of hydroxyalkylation of benzene with propylene oxide as a model reaction.

1.5 Scope of Study

In this research, Al-MCM-41 was synthesized by direct and secondary means using sodium aluminate as the source of aluminium. Through both methods of syntheses, aluminium was substituted for silicon in the framework and on the surface. The insertion of aluminium into the framework of MCM-41 creates acid sites. The structure and physical properties of catalyst were studied by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), ^{27}Al and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance, (^{27}Al and ^{29}Si MAS NMR), Nitrogen Adsorption and Surface Area Analyzer. The acid properties of catalyst were characterized using Temperature Programmed Desorption of Ammonia (TPD-NH_3) and Pyridine Adsorption Measurement. Al-MCM-41 was tested to catalyse the hydroxyalkylation of benzene and propylene oxide; chosen as a model reaction, to produce 2-phenyl-1-propanol. The testing of desired catalyst on the hydroxyalkylation of ethylene oxide and benzene could not be carried out due to the current strict regulation on the import of ethylene oxide. The Friedel-Crafts reactions were carried out which include six main parameters, namely SiO_2:Al_2O_3 ratios, temperature, time on stream, reactant mole ratio composition, solvent and autoclave reactor effect. The products will be characterized by Gas Chromatography and Mass Spectroscopy techniques.

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